

# Solid State Physics Notes

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## **Abstract**

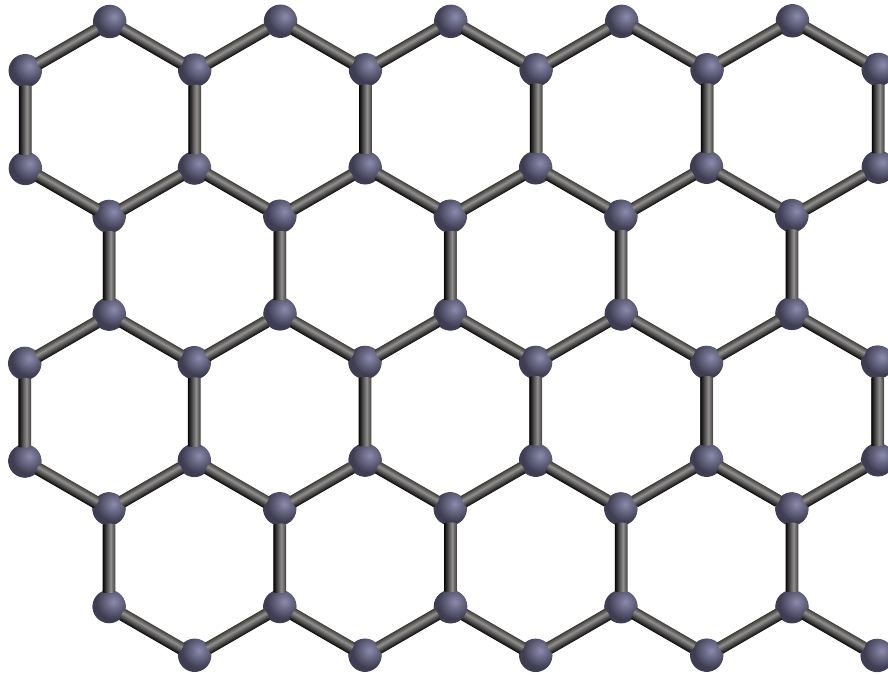
Collected notes of the whole course, base primarily on the course material (i.e. hook and halls book “solid state physics”)

# 1 Crystal Structure

## 1.1 Elementary Crystallography

### 1.1.1 The crystal lattice

The crystal lattice is a way to describe crystal structures. We can take for example graphite as showed in figure 1. In order to create the lattice we take a point in the structure, lets call it  $O$ , then we need to find all identical positions within the structure.

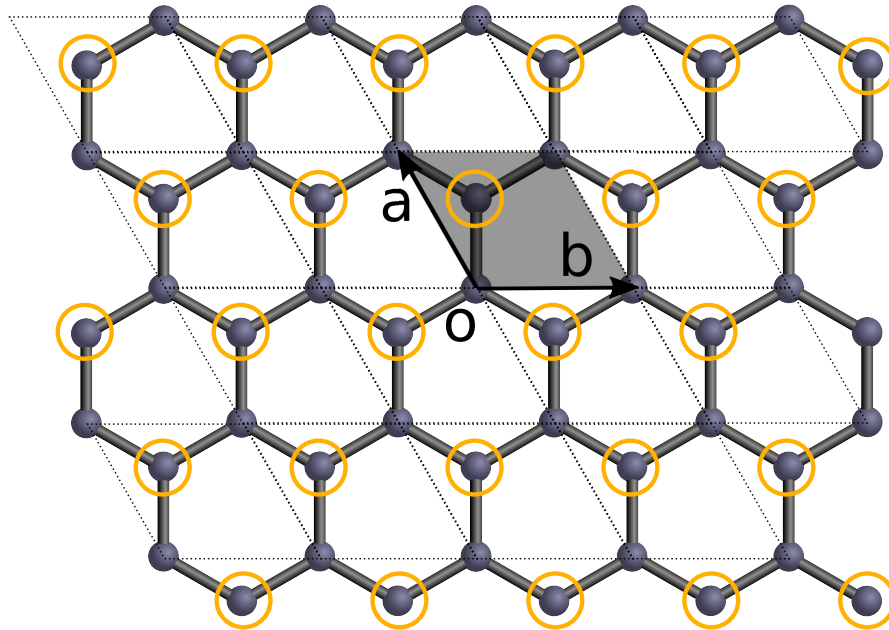


**Figure 1** – Graphite lattice

This choosing of  $O$  and identification of identical position within the structure has been done in figure 2. Using this lattice which is highlighted in the dotted lines we see we have atoms on all lattice points except the atoms circled in yellow. This actually just fine, this is because we define all atoms related to lattice point through something called the basis, which we will look at in section 1.1.3, this means that the crystal lattice do not have to coincide with any atom at all. Using the vectors  $\mathbf{a}$  and  $\mathbf{b}$  here we can define a vector which uniquely defines a point in the lattice relative  $O$

$$\mathbf{r}_{uv} = u\mathbf{a} + v\mathbf{b} \quad (1)$$

All points defined through this equation are together called the **crystal lattice**. An important thing of this lattice is that it possesses **translational invariance**, which basically means that no matter from what lattice point you're looking at, the structure and environment looks precisely the same. For this to hold we need to presume that the lattice is practically infinite, which is something that is generally true.



**Figure 2** – Graphite structure

In three dimension this lattice general arguments extends but the vector that represents all positions in the lattice get an extra term as usual

$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad (2)$$

and instead of getting an area as covered in grey by  $\mathbf{a}$  and  $\mathbf{b}$  in figure 2, we get a volume, a volume we call the **unit cell**.

### 1.1.2 lattice symmetries

The lattice symmetries are usually important when looking at the property of a certain solid. It turns out the available possibilities are quite limited too. We have lattices such as the **rectangular lattice**, **rhombic lattice** and the **centred rectangular lattice**. Look in the book for further explanation.

### 1.1.3 The basis

The basis is what we use to define a position of a particular atom within a lattice. For our example in figure 2 we have vector

$$\mathbf{r}_b = \frac{2}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} \quad (3)$$

that defines the position of the yellow circled atom from a lattice point. But the basis also describes the type of atom, thus we end up with the basis

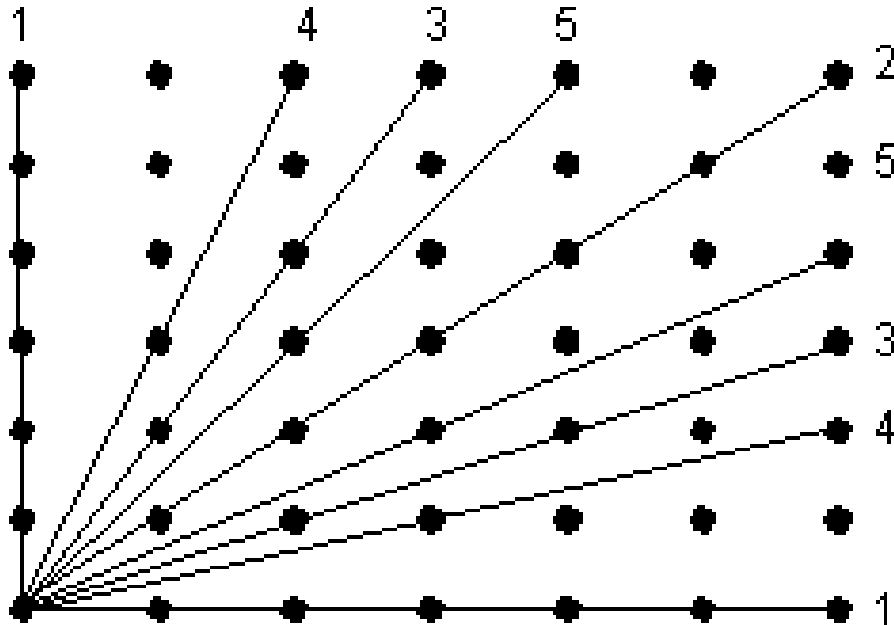
$$C(0,0), C\left(\frac{2}{3}, \frac{1}{3}\right) \quad (4)$$

where the first  $C$  defines the atom at the lattice point, and the second the other atom which was on on the lattice ( $C$  specifies that it is a carbon atom). Likewise for a three dimensional structure we just add one simple term for the position.

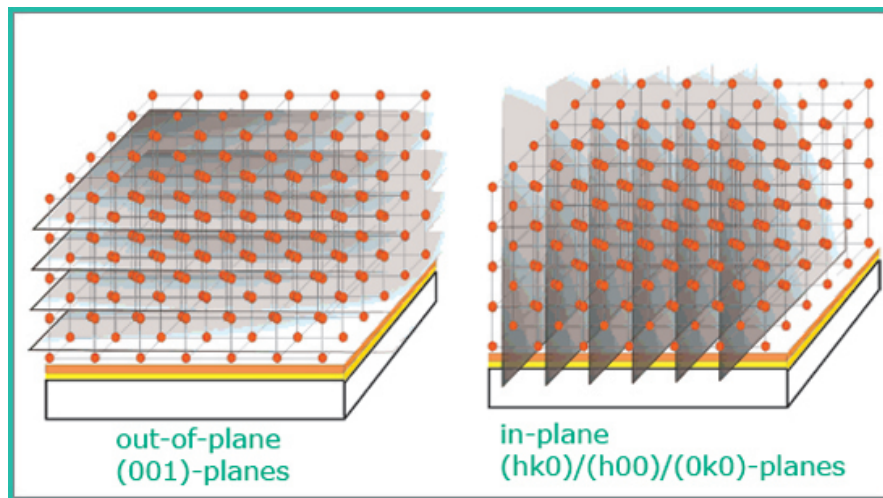
Taking the symmetry of the basis as well as the crystal lattice, we can sort a crystal into one of the 32 possible **point symmetry groups** or **crystal classes** and one of the 230 possible **space symmetry groups**.

### 1.1.4 Crystal planes and directions

Imagine we have a three dimensional rectangular lattice(incidentally called a cubical lattice) that we depict in two dimensions as we have done in figure 3. We can then define a multitude of planes that goes through multiple lattice points. In two dimension it looks simply like lines, but if we stretch that out in three dimensions we can easily see the planes, which is more clearly depicted in figure 4.

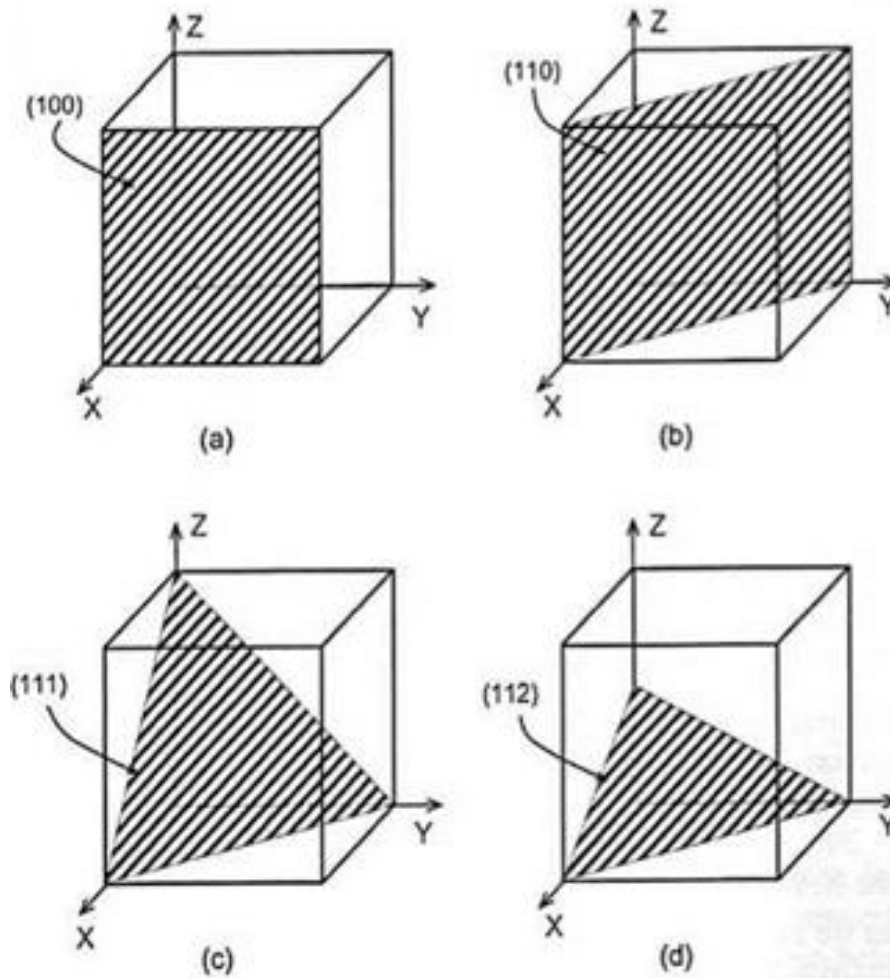


**Figure 3** – Some lattice planes in the cubic lattice, depicted in two dimensions



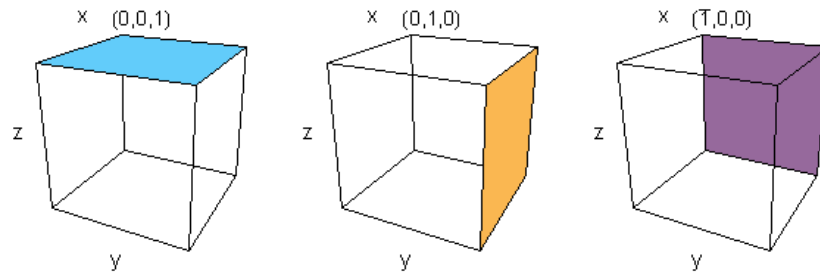
**Figure 4** – Some lattice planes in the cubical lattice, now in 3D!

These lattice planes plays an important role in the diffraction of incoming waves (usually light or more generally an electromagnetic wave). Thus it's important to identify different sets. This is done through **Miller indices**. These indices are defined through where a plane intersects the crystal axes closest to its origin, but not through the origin. By looking at figure 5 we can see four different examples. If we let  $\mathbf{a} = x$ ,  $\mathbf{b} = y$  and  $\mathbf{c} = z$  we can see how in (d) how we have a plane that intersects the crystal axes at  $(\frac{a}{1}, \frac{b}{1}, \frac{c}{2})$ . The Miller Indices is then the reciprocal of these factors we multiply the crystal axes with in order to find the intersect point, it's written as (112). if a plane is parallel to a particular axis it's taken at a zero.



**Figure 5** – Some lattice planes in the rectangular lattice, visually in 3d!

We should also note that from an atomic view a certain amount of planes could due to symmetry in the crystal lattice be equivalent to each other. This is depicted in figure 6. All these three planes are said to belong to the **form**  $\{100\}$ .



**Figure 6** – These lattice planes is equivalent from an atomic point of view, thus all these three are written as belonging to the form  $\{100\}$

One often want to specify the directions of a vector  $\mathbf{r}$  in a crystal. A vector can be written as

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad (5)$$

We then refer to it as the  $[uvw]$  direction. Due to symmetry in cubic crystals the  $[uvw]$  direction is actually the normal to the  $(uvw)$  plane. It should however be noted that this an exception and only hold for lattices with the particular symmetries of the cubic lattice.

## 1.2 Typical crystal structures

Imagine that the atoms act like spheres, so if we wanna tightly pack them it's like packing cannon balls<sup>1</sup>. This is depicted in figure 7. The layer depicted can be stacked upon with another layer with spheres in the A,B or C positions. Now packing the other layer on the A position is neither stable nor efficient, and something that generally don't happen in nature. But depending on how the stacking structure looks like in an atom the solid gets a different structure which can be described by different lattices.

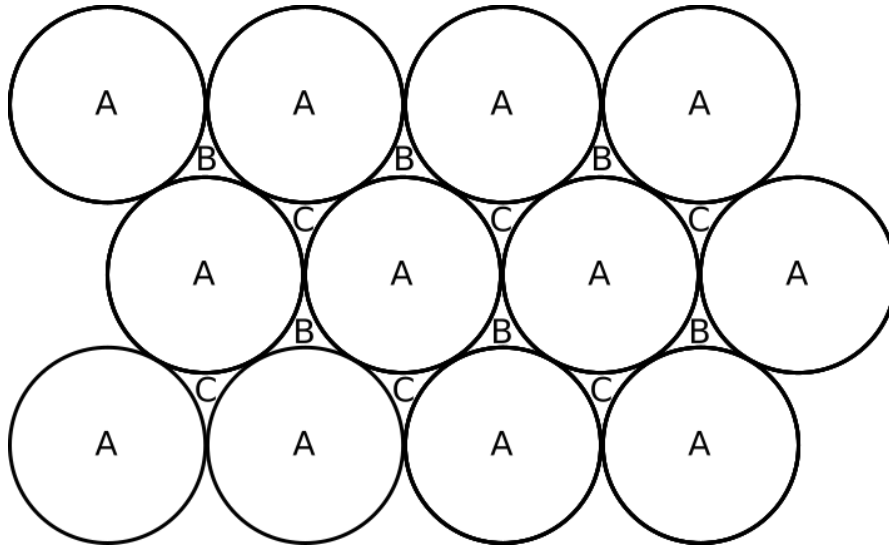


Figure 7 – packed spheres! in 2d!

### 1.2.1 Cubic and hexagonal close-packed structures

The ABCABC... stacking yields the **face-centred cubic** structure, its conventional non-primitive unit cell is depicted in figure 8.

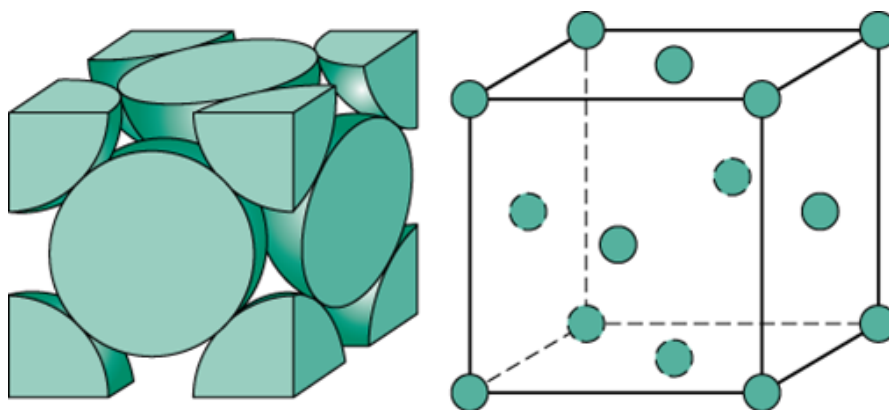


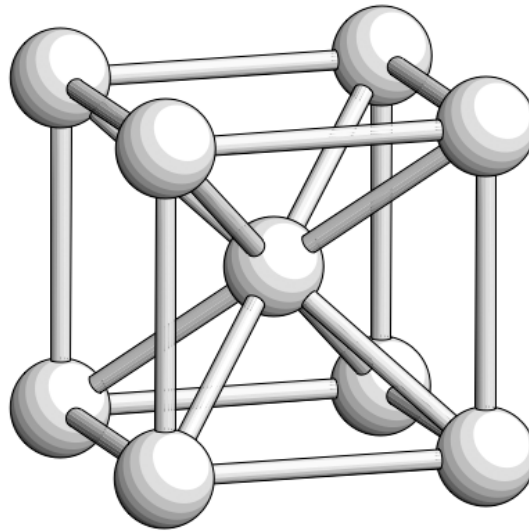
Figure 8 – The face centred cubic

<sup>1</sup>This is actually very close to the truth since the atoms interact with each other with a force that is radial.



### 1.2.2 The body-centred cubic structure

The body centred cubic structure is not quite close packed, so has no real equivalent to the packing sequence as the fcc does. This is due to certain positions are missing in this structure. In reality we can defend this lack of atoms due to the repelling forces among the atoms. The structures conventional non-primitive cell is depicted in figure 9.



**by Dan Shim**

**Figure 9** – The body centred cubics non-primitive conventional cell

### 1.2.3 Structures of ionic solids

Ionic solids are simply a crystal containing more than one element (or a specific type of an atom as we will more specifically look at). In figure 10 we can see atomic structure of the NaCl molecule. Electrons in the negatively charged anion (Cl) are generally less tightly bound than those in the positively charged cation (Na). By convention we write the loosely bound anion as the bigger atom in our structure.

It's interesting to note that we have (111) planes in this lattice as showed here which will create planes of only Na or Cl atoms. That can be showed through its diffraction properties.

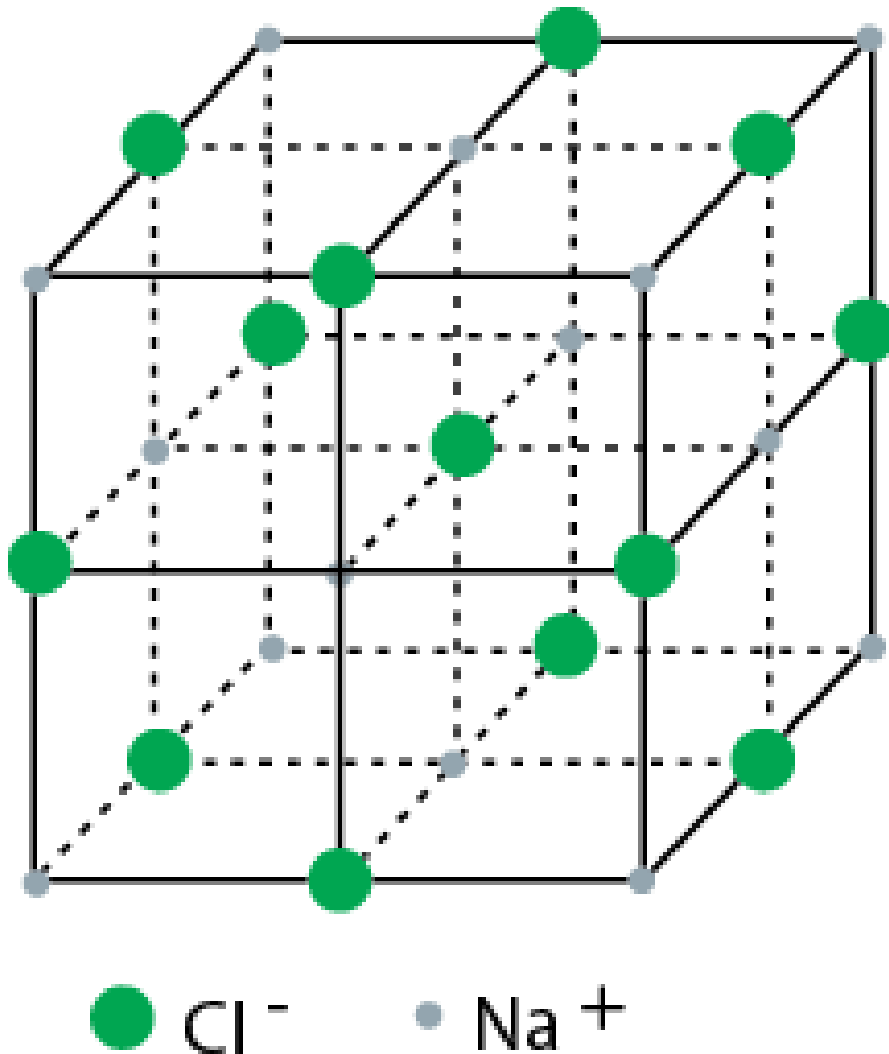
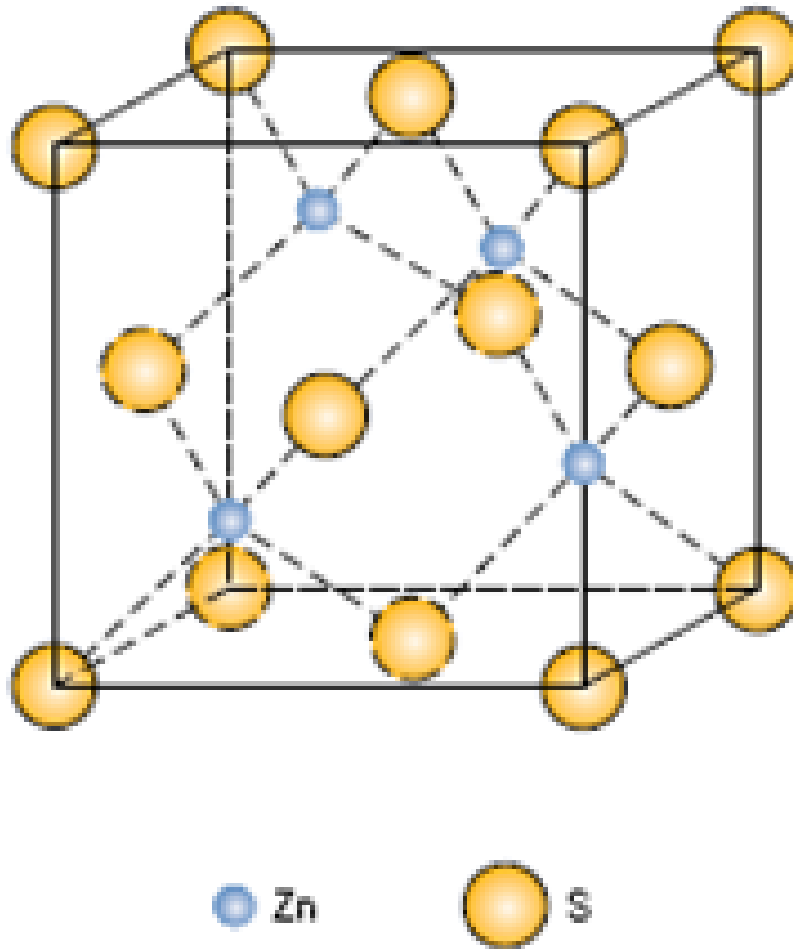


Figure 10 – The ionic structure of the NaCl solid

#### 1.2.4 The diamond and zincblende structures

A more advanced structure which basically can be constructed through a cubic lattice and a more complex basis. This structure is showed in figure 11. It's interesting that the structure is identical for zincblende and diamonds, the only difference is that diamonds are only carbon, while zincblende is made from zinc and sulfur.



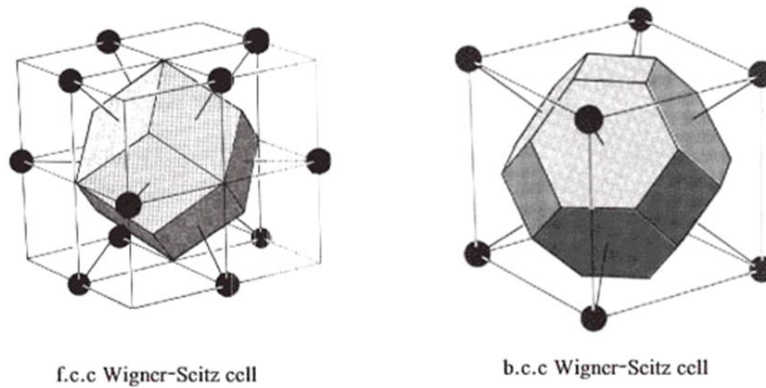
**Figure 11** – The structure for zincblende. Note that it's the same for diamonds except for diamonds you only have carbon

### 1.2.5 The Wigner-Seitz cell

By taking the planes that goes perpendicularly through all the bisects of the lines to an atoms neighbours, one end up with its Wigner-Seitz cell. This represents the "sphere of influence". For the fcc such a cell has twelve neighbours and twelve faces, thus all the sites in fcc has a **coordination number** of twelve.

Always a primitive cell.

## Wigner-Seitz Cell - 3D



Crystal Structure

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**Figure 12** – The Wigner-Seitz cell for the fcc and bcc structure

### 1.3 X-ray crystallography

#### 1.3.1 The Bragg law

Bragg law is a simplified way of looking at the reflection from crystal structures. Instead of using the general laws of diffraction as von Laue did, we will just see lattice planes as "reflective planes". One can then use Bragg's law to help identify crystal structures

$$2d \sin \theta = n\lambda \quad (6)$$

We can have reflections of higher orders ( $n > 1$ ). If we for instance get a reflection of the third order from the plane (111) we call it through convention the reflection of plane (333). In general terms a  $n$ th order reflection of a plane ( $hkl$ ) is written as a reflection from plane ( $nh \ nk \ nl$ ).

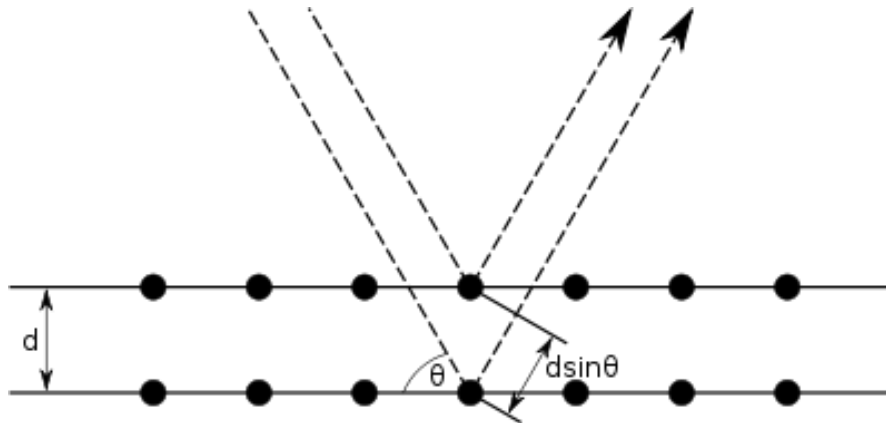
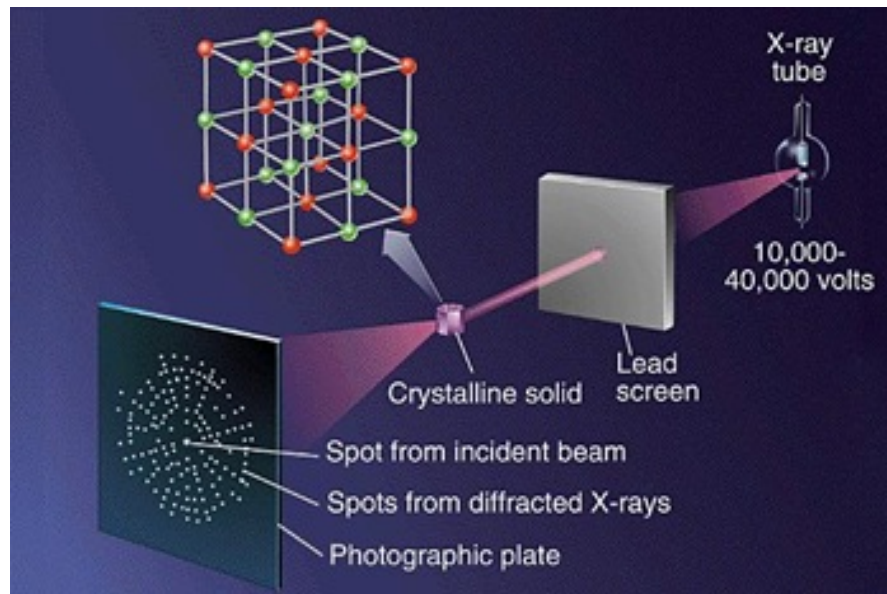


Figure 13 – The reflection due to lattice planes

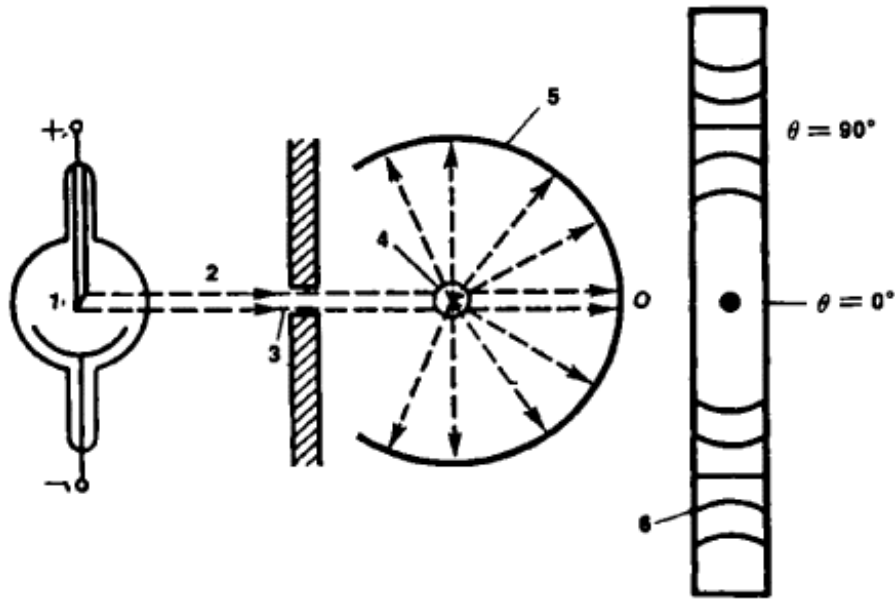
#### 1.3.2 Experimental arrangements for x-ray diffraction

A **Laue photograph** is depicted in figure 14. It is usually a good at showing symmetries, thus a good tool for figuring out the orientation of a crystal.



**Figure 14** – The experimental setup for the Laue photograph

A **Rotating crystal and powder photograph** is depicted in figure 15. It's a tool better suited for analysing the actual structure of a crystal.

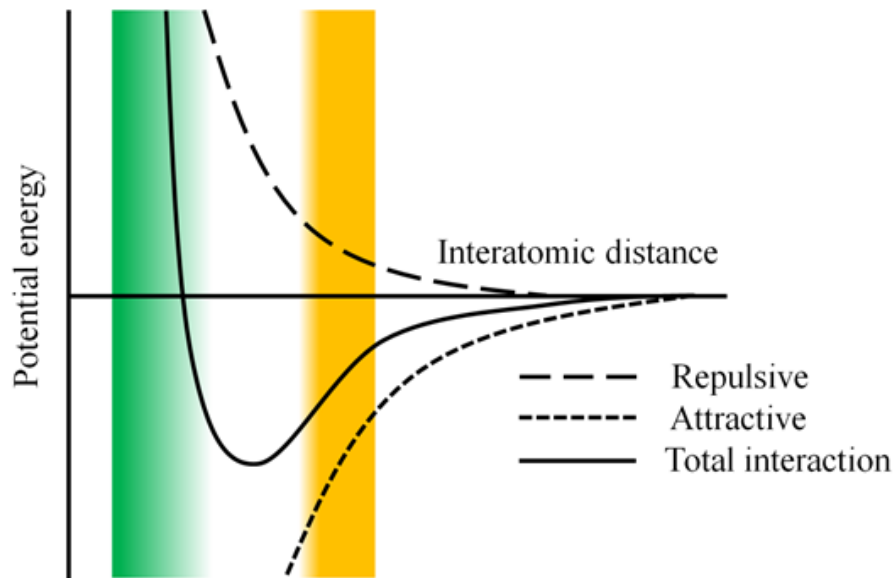


**Figure 15** – The basic setup for a rotating crystal photograph or powder photograph. The difference is whether or not the specimen in the middle is a rotating crystal or a powder of crystalline crystals.

## 1.4 Interatomic forces

### 1.4.1 Van der Waals bonding

Van der Waals occurs with even stable atoms, those who has all the outer electrons in their shell. This is due to fluctuation that creates an electric dipole moment. This force experienced is described by the Lennard-Jones potential depicted in figure 16. Worth noting that the repulsive force is a consequence of the Pauli principle, that states that no two electrons can occupy the same state, and instead the electrons get excited to higher state if another one would come close. This creates a large repulsive force which one clearly see in the Lennard-Jones potential.

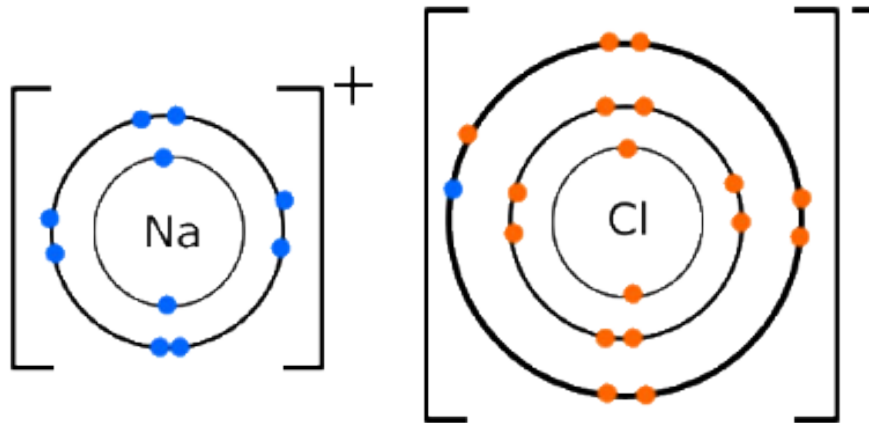


**Figure 16** – The Lennard-Jones potential is the main force in Van der Waals bonding. The color green represent a distance in which repulsion occurs, while the color of orange represents a distance of attraction. Kinda like how it is with us humans too lol.



### 1.4.2 Ionic bonding

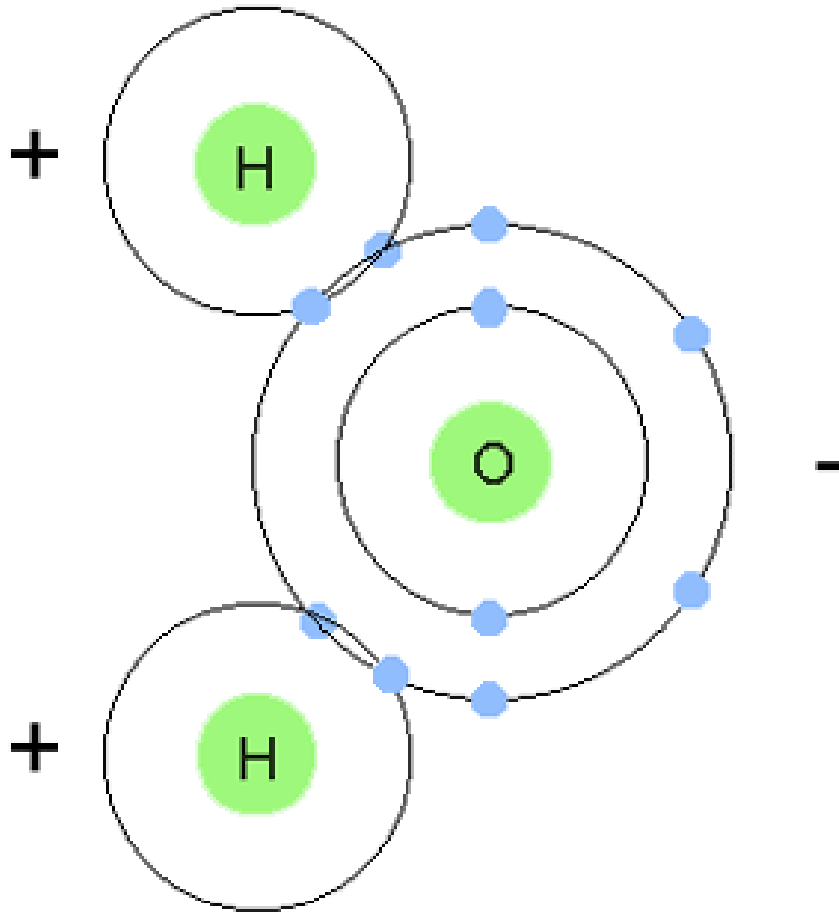
Basically ionic bonding is the process of atoms sharing one electron in order to create two charged atoms with completed outer shells. The truth goes of course down too Schrödinger's, but in this is as far as we go to it now.



**Figure 17** – The ionic bond between Na and Cl. In this example Na gives away its stray atom in its outer shell in order to complete the outer shell of Cl. The reality is more complex, but deeply related to electron states in the shells.

### 1.4.3 Covalent bonding

The covalent bonding is similar to the ionic bonding in the sharing of electrons. The covalent bond has some more complexity related to it. It's usually directed too, so can, among other things, be a factor of why there exists solids which has more complex structures. Basically atoms can share electrons between multiple atoms in order for all the outer shells to be saturated. This is depicted in figure 18 for the famous  $H_2O$  molecule.



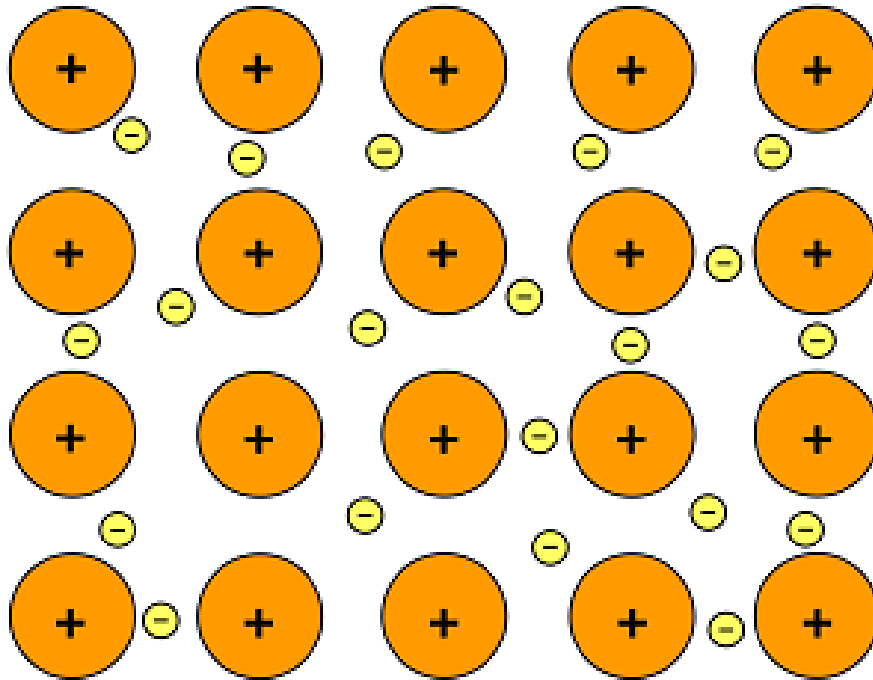
**Figure 18** – The covalent bond is similar to the ionic bond, but shares multiple electrons, could be over multiple atoms and those usually have some kind of direction related to it.

### 1.4.4 Hydrogen bonding

Looking at the earlier picture of the  $H_2O$  molecule in figure 18, we can see that the molecule itself has a negative and positive charge. This causes important bindings in ice and many organic solids.

### 1.4.5 Metallic bonding

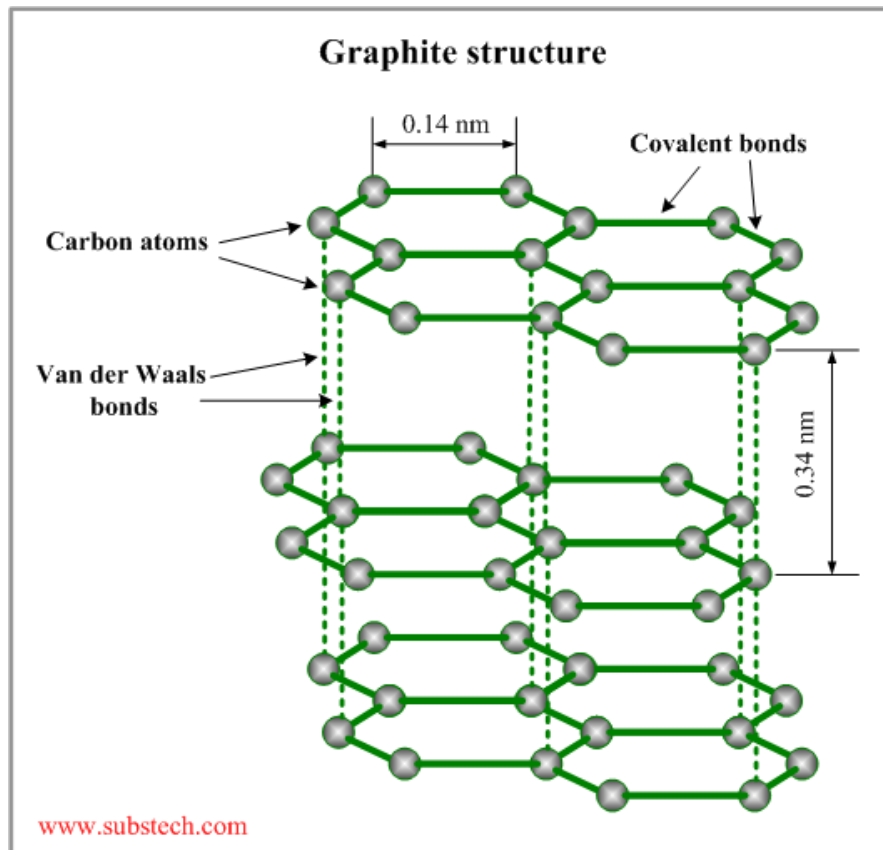
In the metallic bond we have a kind of covalent bond which does not saturate the outer shell of the atoms. This results in "wandering atoms" as depicted in figure 19. This in turns facilitate the ability to conduct electricity.



**Figure 19** – In the metallic bond the atoms share their electrons more freely

### 1.4.6 Mixed bonding

Basically just highlighting that we can have more than one bond in a solid. As an example we have graphite as depicted in figure 20. There we have both a covalent bond in the layer, as well as a Van der Waals bond between layers. This causes graphite to have the interesting effect of only conducting electricity in the direction parallel to the layers, not perpendicular to it (and thus the Van der Waals bond does not conduct electricity especially well).



**Figure 20** – Depicting the mixed bond inside graphite. Each layer has strong covalent bond, while between layers only Van der Waals forces keeps it together.

## 1.5 New Words

- crystal lattice
- translational invariance
- unit cell
- rectangular lattice
- rhombic lattice
- centred rectangular lattice
- point symmetry groups
- crystal classes
- space symmetry groups
- Miller indices
- face-centred cubic
- coordination number

## 2 Waves in crystals

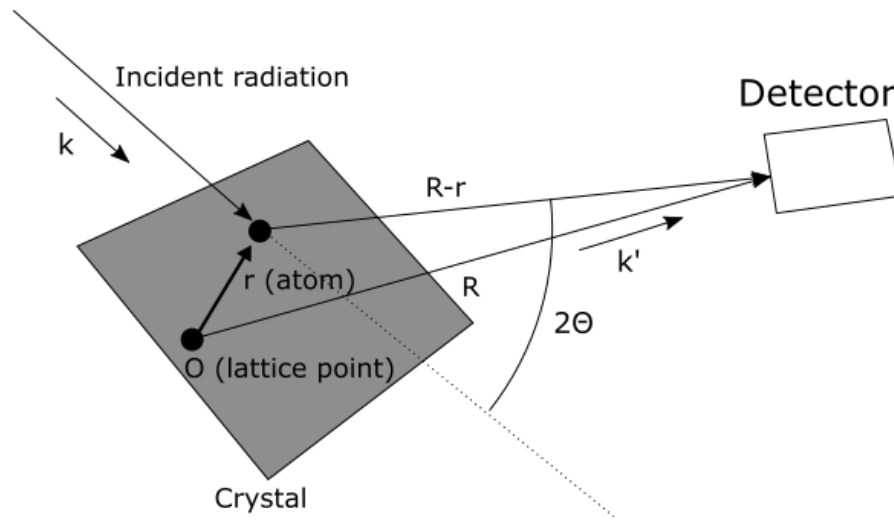
### 2.1 Elastic scattering of waves by a crystal

#### 2.1.1 Amplitude of the scattered wave

Using braggs law we were able to find where we should have reflections. But we know nothing of the amplitude. This we will find out by examining every atom as a point source for radial radiation. This radial radiation gets created when excited, or radiation has hit it. The setup for this thought process is depicted in figure 21.

Lets assume the incident radiation is a plane wave on the form  $A_0 \exp[i((k) \cdot \mathbf{r} - \omega t)]$ . The resulting amplitude of the radiation at the detector is then

$$A_r = A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \times f \times \frac{e^{ik(|\mathbf{R} - \mathbf{r}|)}}{|\mathbf{R} - \mathbf{r}|}. \quad (7)$$



**Figure 21** – An incoming plane wave towards a crystal and description of what part radial excitation wave will hit the detector

We can see three terms in the right hand side of this equation. We will number them as they appear in the equation. The first part is just the incoming wave. The second part is the **atomic form factor** or **atomic scattering factor**, which defines how much radiation a certain atom will scatter. The third term is the amplitude decrease and phase change due to the position of an atom. Assuming that the distance of the detector from the crystal is insanely much larger then the crystal atom distances we can simplify the third term to be

$$\frac{e^{ik(|\mathbf{R} - \mathbf{r}|)}}{R}. \quad (8)$$

We go on to define the **scattering vector K** as

$$\mathbf{K} = \mathbf{k}' - \mathbf{k} \quad (9)$$

We can also apparently sag that  $k \cdot |\mathbf{R} - \mathbf{r}| \approx \mathbf{k}' \cdot (\mathbf{R} - \mathbf{r})$ . So we end up with a term for the amplitude as

$$A_r \approx A_0 \frac{e^{i(k\mathbf{R} - \omega t)}}{R} f e^{-i\mathbf{K} \cdot \mathbf{r}} \quad (10)$$

The first term in this equation is the same for all atoms in a structure, so it can be factored out as a constant. We are left with knowing that the amplitude is proportional to

$$A = \sum_n f_n e^{i\mathbf{K} \cdot \mathbf{r}_n} \quad (11)$$

where the sum is over all atoms in the crystal.

Recalling that the position of an atom can be made up of lattice point position and its basis inside that we can split  $\mathbf{r}$  into its lattice association  $\mathbf{r}_l$  and position relative to the lattice point (using the basis)  $\mathbf{r}_p$ . This idea is depicted in figure 22. The equation then becomes

$$A = \sum_l e^{i\mathbf{K} \cdot \mathbf{r}_l} \times \sum_p f_p e^{i\mathbf{K} \cdot \mathbf{r}_p} \quad (12)$$

The first part of this right hand expression is what determines the direction for which diffraction occurs and is due to the crystal lattice. The second part is due to the basis, and is the same for all lattice points, which is a sum over relatively few atoms. This second part is called the **structure factor**.

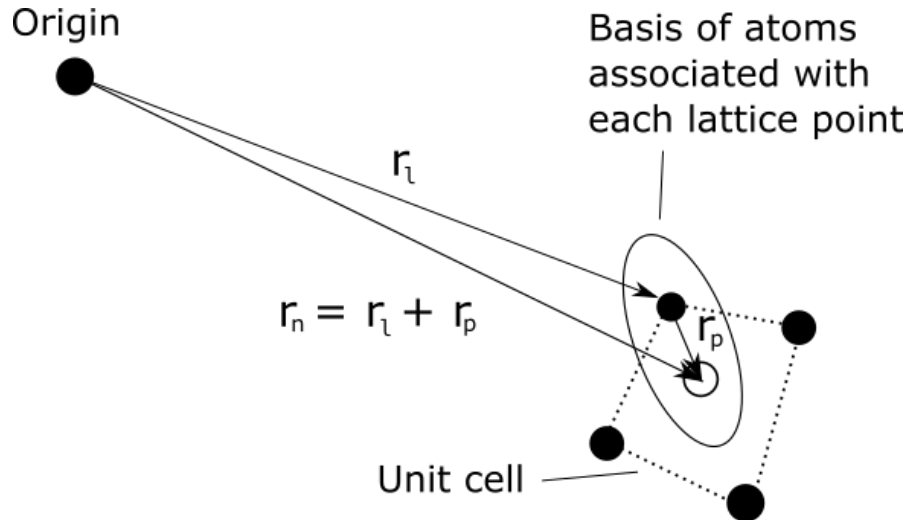


Figure 22

### 2.1.2 Laue conditions for diffraction and the reciprocal lattice

Using equation 2 for the crystal lattice, and the first term in equation 12 we get

$$\sum_l e^{i\mathbf{K}\cdot\mathbf{r}_l} = \sum_u e^{i\mathbf{K}\cdot\mathbf{a}u} + \sum_v e^{i\mathbf{K}\cdot\mathbf{b}v} + \sum_w e^{i\mathbf{K}\cdot\mathbf{c}w}. \quad (13)$$

Since we only get a large scattering amplitude when the contribution from all the lattice point are in phase, we get the requirement that

$$\mathbf{K} \cdot \mathbf{a} = 2\pi h \quad (14)$$

$$\mathbf{K} \cdot \mathbf{b} = 2\pi k \quad (15)$$

$$\mathbf{K} \cdot \mathbf{c} = 2\pi l \quad (16)$$

where  $h, k, l$  is integers. This is what we call the **Laue conditions** for diffraction. When these requirements are satisfied we get unity from the lattice term in amplitude for every lattice point and we end up with the number of primitive unit cells as the lattice term.

The directions of the diffracted beams are thus given by the set of vectors  $\mathbf{k}$  that satisfies the Laue conditions. It turns out that this set of vectors are actually the reciprocal of the lattice vectors! I.e.

$$\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (17)$$

where

$$\begin{aligned} \mathbf{a}^* &= \frac{2\pi(\mathbf{b} \times \mathbf{c})}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\ \mathbf{b}^* &= \frac{2\pi(\mathbf{c} \times \mathbf{a})}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\ \mathbf{c}^* &= \frac{2\pi(\mathbf{a} \times \mathbf{b})}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \end{aligned} \quad (18)$$

The book proves in page 321 that bragg's and these requirements both hold up.

Since the scattering vector of each diffracted beam corresponds to a point in reciprocal lattice, we can use the integers  $h, k, l$  to label the beams. These labels are identical to the miller indices of the lattice plane that is associated with the diffracted beam, this is also proved in the book at page 321.

To surmise: for an incident radiation of wavevector  $\mathbf{k}$ , the direction of the diffracted beams are given by wavevectors  $\mathbf{k}' = \mathbf{k} + \mathbf{K}$ , where the scattering vector  $\mathbf{K}$  is any one of the points of the reciprocal lattice for the crystal. You determine the  $\mathbf{K}$  vector through equations 18.

### 2.1.3 Examples of reciprocal lattices

In describing these reciprocal we will use the three mutually perpendicular real value unit vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}$ .

**The simple cubic real space lattice** is going to be investigated first! In terms of Cartesian axes we have

$$\begin{aligned} \mathbf{a} &= a\mathbf{i} \\ \mathbf{b} &= a\mathbf{j} \\ \mathbf{c} &= a\mathbf{k} \end{aligned} \quad (19)$$



using equation 18 we get the reciprocal

$$\begin{aligned}\mathbf{a} &= \frac{2\pi}{a} \mathbf{i} \\ \mathbf{b} &= \frac{2\pi}{a} \mathbf{j} \\ \mathbf{c} &= \frac{2\pi}{a} \mathbf{k}\end{aligned}\tag{20}$$

Basically just the same with shorter sides!

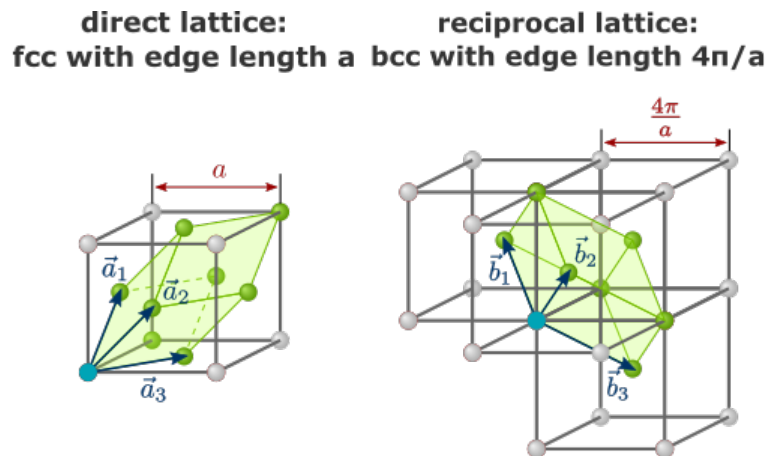
**The face-centred cubic real space lattice** is intriguingly connected with the bcc. We start with define the fcc as

$$\begin{aligned}\mathbf{a} &= \frac{a}{2}(\mathbf{j} + \mathbf{k}) \\ \mathbf{b} &= \frac{a}{2}(\mathbf{k} + \mathbf{i}) \\ \mathbf{c} &= \frac{a}{2}(\mathbf{i} + \mathbf{j})\end{aligned}\tag{21}$$

which gives us the reciprocal

$$\begin{aligned}\mathbf{a} &= \frac{2\pi}{a}(\mathbf{j} + \mathbf{k} - \mathbf{i}) \\ \mathbf{b} &= \frac{2\pi}{a}(\mathbf{k} + \mathbf{i} - \mathbf{j}) \\ \mathbf{c} &= \frac{2\pi}{a}(\mathbf{i} + \mathbf{j} - \mathbf{k})\end{aligned}\tag{22}$$

Which yields the bcc! Not completely visible perhaps, maybe easier to see through the reciprocal equations directly perhaps. But basically the vectors get translated around to the bcc, and scaled of course, this is depicted in figure 23.



**Figure 23** – Here we can see how the reciprocal of the fcc lattice is just rotated and scaled into a bcc lattice

### 2.1.4 The structure factor

Now it's time we look at the second part of equation 12. This part

$$S = \sum_p f_p e^{-i\mathbf{K} \cdot \mathbf{r}_p} \quad (23)$$

is known as the structure factor and only concerns the basis in the structure.

**The simplest form** of structure factor occurs when we only have one atom at each lattice point. This then reduces to be

$$S = f \quad (24)$$

where  $f$  is only dependent on the incident angle and what kind of atoms that occurs on the lattice.

Using the hexagonal close packed structure, as depicted in figure 24, we get another basis

$$\mathbf{r}_1 = \mathbf{0} \quad (25)$$

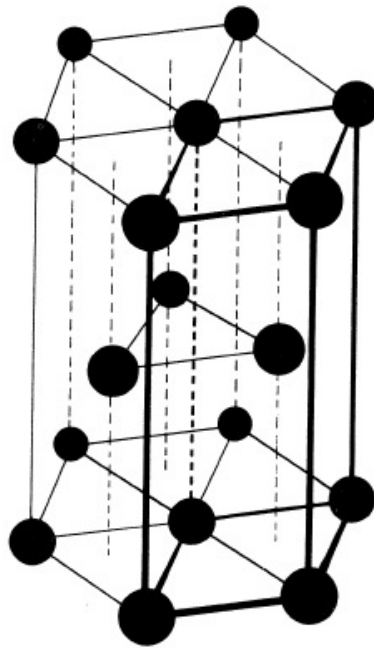
$$\mathbf{r}_2 = \mathbf{a}/3 + \mathbf{b}(2/3) + \mathbf{c}/2 \quad (26)$$

So if we put this into the structure factor equation 23 and use the reciprocal equation 18, we get

$$S = f\{1 + \exp[-i\pi((h+k+l) + (k-h)/3)]\} \quad (27)$$

Since the amplitude is proportional to  $S$ , we can use this equation to do some analysis of where the amplitude might completely go to zero. But also to some extent see which planes will have a large contribution to reflections. This of course have to weighted against the lattice term as well.

We also have to note we haven't looked into the atomic factor at all. It could differ for the same atoms as well due to different environment and such. This have an effect on structures like the diamond.



**Figure 24** – The hexagonal close packed structure.

## 3 Diamagnetic and paramagnetism

### 3.1 Introduction

The increase in a magnetic field applied to any material (referred to as  $\mathbf{H}$ ) causes an induced electromotive force, which in turn accelerates electrons in the material. Then according to Lenz's law the resulting electric current is such that it reduces the magnetic field applied inside the material, one also say that the magnetic field is "screened" from the material.

What's more interesting is that this current actually still exist even if the magnetic field is held at a constant value<sup>2</sup>. If this does indeed happen in a material, then the material is *diamagnetic*. Note that the current creates a magnetic field, Denoted as  $\mathbf{M}$ , which works against the applied magnetic field,  $\mathbf{H}$ .

If a material posses atoms with a permanent magnetic dipole moment<sup>3</sup>, then the diamagnetic effects are usually very small in comparison to the *paramagnetic* effects. The paramagnetic effect creates a magnetization,  $\mathbf{M}$ , which works with the applied magnetic field,  $\mathbf{H}$ .

We can relate the magnetization of the material,  $\mathbf{M}$ , with the applied magnetic field,  $\mathbf{H}$  through the *magnetic susceptibility*,  $\chi$ , of the material as

$$\mathbf{M} = \chi \mathbf{H}. \quad (28)$$

From this we can deduce the sign of the magnetic susceptibility will be positive for paramagnetic materials and negative for diamagnetic materials.

### 3.2 Paramagnetism

#### 3.2.1 The origin of permanent dipole moments

From ampere's law we can deduce an equation for the magnetic dipole moment,  $\boldsymbol{\mu}$ , to be

$$\boldsymbol{\mu} = i \mathbf{a}. \quad (29)$$

Where  $\mathbf{a}$  is the area vector of the loop, directed so that the current is clockwise when looking along  $\mathbf{a}$ . and  $i$  is the electric current.

To start with we can look at the dipole moment of a electron going around it's nucleus with a period of  $\tau$ , and a radius  $r$ . The current is then

$$i = (-e)/\tau = -ev/2\pi r. \quad (30)$$

Where the negative sign comes from the fact that the electron moves in the opposite direction of the current<sup>4</sup>. Rewriting the dipole moment with this current we get

$$\boldsymbol{\mu} = -\frac{ev}{2\pi r} \mathbf{a}. \quad (31)$$

Now we can use the angular momentum of the electron which is  $\hbar \mathbf{I}$ . The  $\hbar$  is just convention, as we know constants can be multiplied in and divided away as long as it's done in a

---

<sup>2</sup>We will explain this phenomenon later.

<sup>3</sup>Think bar magnets.

<sup>4</sup>Thank you convention for making everything confusing!

balanced matter. If we see that  $|\mathbf{a}| = \pi r^2$ ,  $|\hbar| = mvr$  and that  $\mathbf{a}$  and  $\mathbf{I}$  is directed in the same direction, we can rewrite the dipole moment as

$$\boldsymbol{\mu} = -\frac{e\hbar}{2m}\mathbf{I}. \quad (32)$$

We can then define the constant part as the Bohr magneton,  $\mu_B$ , i.e.

$$\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} JT^{-1}. \quad (33)$$

Now we've used the classical model of an electron spinning around its nucleus to figure out the dipole moment contribution due to the orbital angular momentum of the electron through equation 32. But due to hand waviness, we're gonna go the quantum mechanical route with this equation. Thus we have an equation

$$\boldsymbol{\mu} = -\mu_B\mathbf{I} \quad (34)$$

for the orbital angular momentum, but also a magnetic dipole moment is given for the spin in the quantum mechanical treatment that is as follows

$$\boldsymbol{\mu}_{spin} = -g_0\mu_B\mathbf{S}. \quad (35)$$

And we estimate  $g_0 = 2^5$  and we get a total magnetic dipole moment to be

$$\boldsymbol{\mu} = -\mu_B(\mathbf{L} + 2\mathbf{S}). \quad (36)$$

Where  $\mathbf{L}$  is the total sum of atoms electron orbital momentums and  $\mathbf{S}$  is the sum of the atoms electrons spin angular momenta. For every closed shell this sum adds up to be zero. Thus permanent dipole moments only occur in atoms or ions with an incomplete shell.

To look at how an incomplete shell is built for incomplete shells in isolated ions, and thus being able to calculate the momenta of them, we use the Russell-Sounders coupling scheme, or L-S coupling. It states that the stationary states of the shell are eigenstates of  $\mathbf{L}^2$ ,  $\mathbf{S}^2$  and  $\mathbf{J}^2$ , with eigenvalues  $L(L+1)$ ,  $S(S+1)$  and  $J(J+1)$ . To find the values of L,S and J we use the Hund's rules

1. S takes the maximum value allowed by the exclusion principle, thus as many as possible of the electrons have parallel spins
2. L takes the maximum value consistent with this value of S - the electrons have their orbital angular momenta as well aligned as possible
3.  $J = |L - S|$  for shells less then half full and  $J = L + S$  for shells more then half full.

Here it's interesting to note that rule 1 and 2 of Hund's rules are closely associated with the Coulomb forces between electrons, due to them being much larger then the magnetic force<sup>6</sup>. And the value of j, is associated with the spin-orbit interaction, that is with the magnetic field generated by the motion of the electrons within the atom, this is of order  $10T^7$ . So the 3rd rule can be effected by a field applied of this order.

In figure 25 we get a picture of two ions having applied the Hund's rule on to determine the values of L,S and J.

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<sup>5</sup>Sorry, too intricate to explain

<sup>6</sup>Not argued for here, but take my word for it!

<sup>7</sup>Also just a given fact

	$V^{3+}$	$Fe^{2+}$
Number of 3d electrons	2	6
Occupancy of states as given by Hund's rules		
Hund's rule 1: determination of $S$ . Make as many spins parallel as possible	$S = \frac{1}{2} + \frac{1}{2}$ $= 1$	$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2}$ $= 2$
Hund's rule 2: determination of $L$ . Make $\sum l_z$ as large as possible	$L = \sum l_z$ $= 2 + 1 = 3$	$L = 2 + 1 + 0 - 1 - 2 + 2$ $= 2$
Hund's rule 3: determination of $J$ .	$\leq ?$ Shell less than half-full $J =  L - S  = 2$	Shell more than half-full $J = L + S = 4$
Spectroscopic notation, $^{2S+1}L_J$	$^3F_2$	$^5D_4$

Fig. 7.2 Use of Hund's rules to calculate the quantum numbers  $S$ ,  $L$  and  $J$  of the ground states of the  $V^{3+}$  and  $Fe^{2+}$  ions. The 3d shell has  $l = 2$  so there are  $2l + 1$  sublevels corresponding to  $l_z = -2, -1, 0, 1, 2$  as indicated. In the spectroscopic notation, values of  $L$  of 0, 1, 2, 3, 4, 5, 6, ... are indicated by letters S, P, D, F, G, H, I, ...

Figure 25 – Copied from Solid State Physics by J.R. Hook and H.E. Hall

### 3.2.2 The interaction of permanent dipole moment with an applied magnetic field

Alignment of an atomic dipole by a field  $\mathbf{B}$  (which is taken to be along the z-axis) occurs because of an energy term in the electrons,  $H_P$ ,

$$H_P = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B. \quad (37)$$

Where  $\boldsymbol{\mu}$  is given by equation 36. It should however be noted that you should not think of it as an atomic bar magnet, because things does not quite act the same on the atomic level as things does in the macroscopic world<sup>8</sup>. For instance this  $H_P$  energy is actually part of the kinetic energy of the atom.

<sup>8</sup>But of course it does now just to be confusing.

If we assume that the energy  $H_p$  is small, we can use first-order perturbation theory to calculate the effect of the alignment energy. We then assume a ground state (nothing excited to a new level) for the ion, or atom, and use quantum hand waviness to get the expectation energy

$$E_p = \langle H_p \rangle = g\mu_B J_z B \quad (38)$$

where  $j_z = -j, \dots, 1, 0, 1, \dots, j$  and  $g$  is the *Landé g-factor*

$$g = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)} \quad (39)$$

Comparing equation 37 and equation 38, we can see that we seem to have an effective magnetic moment

$$\mu_{eff} = g\mu_B \mathbf{J} \quad (40)$$

### 3.2.3 Calculation of the magnetization of paramagnetic ions

Now, finally, we have the energy which is due to the magnetic dipole moment in the electrons, maybe we could calculate the magnetization from the paramagnetic material given a certain temperature  $T$  and magnetic field  $\mathbf{B}$ .

Well, if we look at every dipole as they where independent on each other, we can use the Boltzmann factor to figure out how the relative occupation of energy levels will be at a certain temperature  $T$ . The Boltzmann factor is given by

$$e^{-E_p/k_B T} = e^{\mu_{eff} \cdot \mathbf{B}/k_B T} \quad (41)$$

and we did use equation 38 here in order to complete our expression for the Boltzmann factor. We can go one step further and specify that the magnetization field is parallel to the z-axis and the expression becomes

$$e^{\mu_{eff}^z B/k_B T} \quad (42)$$

where

$$\mu_{eff}^z = -g\mu_B J_z. \quad (43)$$

We can then write the net magnetization for  $N$  moments per unit volume, through our deep understanding of statistical physics, to be

$$M = N \sum_{J_z=-J}^{+J} (e^{\mu_{eff}^z B/k_B T} / \sum_{J_z=-J}^{+J} e^{\mu_{eff}^z B/k_B T}) \quad (44)$$

Note that the  $J$  is baked into the  $\mu_{eff}^z$  constant.



Using some fancy rewrites and awesome algebraic skills we can get to another expression that is easier to study, which is

$$M = Ng\mu_B JB_J(x) \quad (45)$$

Where

$$x = g\mu_B B J / k_B T \quad (46)$$

and

$$B_J(x) = \frac{2J+1}{2J} \coth\left[\left(\frac{2J+1}{2J}\right)x\right] - \frac{1}{2J} \coth\left(\frac{x}{2J}\right). \quad (47)$$

Where  $B_J(x)$  is known as the Brillouin function. This function has the interesting property of increasing linearly for small  $x$ , but saturates at 1 for large  $x$ . Thus for small fields applied to a paramagnetic material the resulting magnetization in the material increases linearly to then reach the *saturation magnetization*  $Ng\mu_B J$  when a large field is applied.

For small fields (or rather small  $x$ ) we can approximate  $B_J(x)$  to be

$$B_J(x) \approx \frac{(J+1)x}{3J}. \quad (48)$$

So the resulting magnetization in small fields are

$$M = \frac{Ng^2\mu_B^2 J(J+1)B}{3k_B T} \quad (49)$$

Here we must note that  $B$  is the local field around the dipole, this could differ significantly from the applied field, due to magnetic moments for neighbouring ions. But, for small  $\chi$  we get that the magnetization is way smaller than the applied field, i.e.  $M \ll H$ . So the local field must be dominated by the applied magnetic field. This makes us go back to the ideas of electrostatics and see that the difference between  $\mu_0 H$  and  $B$  must be vanishingly small. Thus for small fields applied to paramagnetic materials we get the susceptibility

$$\chi = \frac{M}{H} = \mu_0 \frac{M}{B} = \frac{Np^2\mu_B^2\mu_0}{3k_B T} \quad (50)$$

where  $p = \sqrt{g[j(j+1)]}$ .

This fits in with the *Curie law* which says that the susceptibility is inversely proportional to the temperature  $\chi = C/T$ . The *Curie constant* in our case becomes

$$C = \frac{Np^2\mu_B^2\mu_0}{3k_B} \quad (51)$$

Putting in some numbers for the susceptibility we find that the difference between  $B$  and  $\mu_0 H$  only becomes relevant when in temperatures around and below 1K. We will not look at cases where the difference actually matters.

**Quenching** is an interesting phenomenon which we can see by comparing the measured values for  $p$  (by measuring the susceptibility for materials) and the theoretical values for  $p$  using Hund's rules. Looking at figure 26 and figure 27, we can see that for most of the transition metals it fits better to use  $S$  in the equation to calculate  $p$  rather than  $J$ . It would seem that the orbital angular momentum is quenched. This is due to something

called the *Crystal field*. This field is an electric field produced by nearby ions in the material. As we talked about earlier, only the third of Hund's rules are affected by this.

So if the crystal field is dominant, which it usually is in transition metals... then the symmetry of the environment is often such that the eigenstates determined by the crystal field have  $\langle L_{xyz} \rangle = 0$ . Thus we have the quenching.

**TABLE 7.1** Values of  $p$  deduced, using Eq. (7.18), from measured values of the Curie constant for rare-earth ions compared with the value,  $g[J(J+1)]^{1/2}$ , predicted for the Hund's rule ground state of the ion. The discrepancies between theory and experiment for Sm and Eu can be accounted for by the existence of levels with different  $J$  values within  $\sim k_B T$  of the ground state

Ion	Number of 4f electrons	Hund's rule ground state	Measured $p$	Calculated $p$
La <sup>3+</sup>	0	<sup>1</sup> S <sub>0</sub>	0	0
Ce <sup>3+</sup>	1	<sup>2</sup> F <sub>5/2</sub>	2.4	2.54
Pr <sup>3+</sup>	2	<sup>3</sup> H <sub>4</sub>	3.5	3.58
Nd <sup>3+</sup>	3	<sup>4</sup> I <sub>9/2</sub>	3.5	3.62
Pm <sup>3+</sup>	4	<sup>5</sup> I <sub>4</sub>	–	2.68
Sm <sup>3+</sup>	5	<sup>6</sup> H <sub>5/2</sub>	1.5	0.84
Eu <sup>3+</sup>	6	<sup>7</sup> F <sub>0</sub>	3.4	0.00
Gd <sup>3+</sup>	7	<sup>8</sup> S <sub>7/2</sub>	8.0	7.94
Tb <sup>3+</sup>	8	<sup>7</sup> F <sub>6</sub>	9.5	9.72
Dy <sup>3+</sup>	9	<sup>6</sup> H <sub>15/2</sub>	10.6	10.63
Ho <sup>3+</sup>	10	<sup>5</sup> I <sub>8</sub>	10.4	10.60
Er <sup>3+</sup>	11	<sup>4</sup> I <sub>15/2</sub>	9.5	9.59
Tm <sup>3+</sup>	12	<sup>3</sup> H <sub>6</sub>	7.3	7.57
Yb <sup>3+</sup>	13	<sup>2</sup> F <sub>7/2</sub>	4.5	4.54
Lu <sup>3+</sup>	14	<sup>1</sup> S <sub>0</sub>	0	0

(The experimental values are from R. Kubo and T. Nagamiya, *Solid State Physics*, McGraw-Hill, New York, 2nd edn (1968), p. 451)

**Figure 26** – Copied from Solid State Physics by J.R. Hook and H.E. Hall

TABLE 7.2 Comparison of experimental and theoretical values of  $p$  for transition metal ions. The experimental values agree much better with  $2[S(S + 1)]^{1/2}$  than with  $g[J(J + 1)]^{1/2}$ , indicating that the orbital angular momentum is quenched

Ion	Number of 3d electrons	Hund's rule ground state	Measured $p$	$g[J(J + 1)]^{1/2}$	$2[S(S + 1)]^{1/2}$
$K^+$	0	$^1S_0$	0	0	0
$V^{4+}$	1	$^2D_{3/2}$	1.8	1.55	1.73
$V^{3+}$	2	$^3F_2$	2.8	1.63	2.83
$V^{2+}$	3	$^4F_{3/2}$	3.8	0.77	3.87
$Cr^{3+}$	3	$^4F_{3/2}$	3.7	0.77	3.87
$Mn^{4+}$	3	$^4F_{3/2}$	4.0	0.77	3.87
$Cr^{2+}$	4	$^5D_0$	4.8	0	4.90
$Mn^{3+}$	4	$^5D_0$	5.0	0	4.90
$Mn^{2+}$	5	$^6S_{5/2}$	5.9	5.92	5.92
$Fe^{3+}$	5	$^6S_{5/2}$	5.9	5.92	5.92
$Fe^{2+}$	6	$^5D_4$	5.4	6.70	4.90
$Co^{2+}$	7	$^4F_{9/2}$	4.8	6.54	3.87
$Ni^{2+}$	8	$^3F_4$	3.2	5.59	2.83
$Cu^{2+}$	9	$^2D_{5/2}$	1.9	3.55	1.73

(The experimental values are from R. Kubo and T. Nagamiya, *Solid State Physics*, McGraw-Hill, New York, 2nd edn (1968), p. 453)

Figure 27 – Copied from Solid State Physics by J.R. Hook and H.E. Hall

### 3.2.4 Conduction electron paramagnetism

TODO FINISH THIS WHEN YOU READ CHAPTER 3 ABOUT FREE ELECTRONS.

### 3.3 Diamagnetic

In the introduction we mentioned a classical effect that generates a screening effect on a changing magnetic field. However, quantum mechanics gives rise to a tendency, in all matter, to give a stable exclusion of applied fields. To understand that we must consider in detail what happens when a charged particle is accelerated by a changing magnetic field.

#### 3.3.1 Momentum in a magnetic field

By going through the example in the book on page 211-213, get an expression of the momentum of a charged particle,  $\mathbf{p}$ , to be

$$\mathbf{p} = M\mathbf{v} + q\mathbf{A} \quad (52)$$

where  $M$  is the mass of the charged particle,  $v$  is the velocity,  $q$  is the charge and  $\mathbf{A}$  is the magnetic vector potential the particle lies in. This expression is obtained through classical means and gives us a sense that charged particles gives us a momentum that not only depends on its velocity and mass, but also the magnetic vector potential the charged particle exists in.

We will now use equation 52 with  $q \rightarrow -e$  and  $M \rightarrow m$  in subsequent subsections.

#### 3.3.2 Screening by induced currents

In the book on page 213-214 an argument is made that the quantum states, as related to momentum, is kind of rigid. It needs a lot of energy to get excited to another state. Thus a large applied field is required to excite the electrons in an atom. But if we assume that the field is not strong enough to do that, we can assume that when you apply a field the momentum  $\langle \mathbf{p} \rangle$  stays constant but the velocity  $\langle \mathbf{v} \rangle$  changes (As described in the previous section). Using equation 52 we get that the induced velocity is

$$\mathbf{v} = \frac{e\mathbf{A}}{m} \quad (53)$$

and the resulting current density to be

$$\mathbf{j} = n(-e)\mathbf{v} = -\frac{ne^2}{m}\mathbf{A} \quad (54)$$

In the book on p. 214 it is shown that the screening effect is small. The characteristic length of the vector potential  $\mathbf{A}$  is two orders of magnitude larger than the atom itself<sup>9</sup>.

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<sup>9</sup>The derivation is made through Maxwell's equations and are quite simple, look at it at your leisure

### 3.3.3 Calculation of the diamagnetic susceptibility

Looking at figure 28 we see a cylindrical system setup so that the  $z$ -axis is parallel to  $\mathbf{B}$  and the origin at the atom.  $\rho$  is the radius and  $B$  is the magnitude of the uniform magnetic field applied. It is given in the book that the uniform field created by this system can be expressed through the vector potential

$$\mathbf{A} = \hat{\mathbf{c}} B \rho / 2 \quad (55)$$

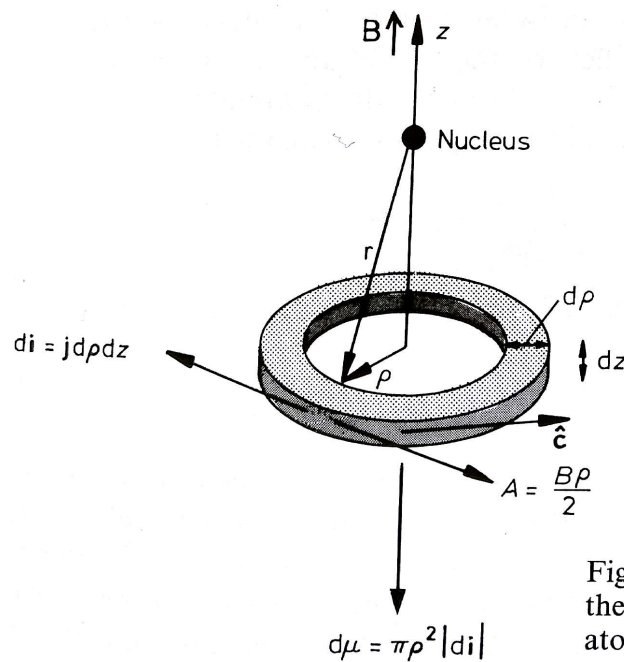


Fig. 7.7 Current element for calculating the magnetic dipole moment  $\mu$  of an atom due to induced screening currents

Figure 28 – Copied from Solid State Physics by J.R. Hook and H.E. Hall

thus, by using equation 54, the current density becomes<sup>10</sup>

$$\mathbf{j} = -\hat{\mathbf{c}} \frac{ne^2 B \rho}{2m}. \quad (56)$$

By assuming that  $n$  is constant within the ring in figure 28, we can write that the current of this ring  $d\mathbf{i}$  is

$$d\mathbf{i} = \mathbf{j} d\rho dz = -\hat{\mathbf{c}} \frac{ne^2 B \rho}{2m} d\rho dz \quad (57)$$

Using amperes law (equation 29) we get that the ring contributes to the dipole moment,  $d\boldsymbol{\mu}$ , as

$$d\boldsymbol{\mu} = -\hat{\mathbf{z}} |d\mathbf{i}| \pi \rho^2 = -\mathbf{B} \frac{e^2 \rho}{2m} \pi \rho^2 d\rho dz. \quad (58)$$

So the total induced moment becomes

$$\boldsymbol{\mu} = -\mathbf{B} \frac{e^2}{4m} \int n \rho^2 dV \quad (59)$$

where  $dV = 2\pi \rho dz$  is the volume of the ring. Since  $\int dV = Z$  where  $Z$  is the number of electrons in the atom we can write  $\int n \rho^2 dV = Z \langle \rho^2 \rangle$ , and we get

$$\boldsymbol{\mu} = -\frac{Ze^2}{4m} \langle \rho^2 \rangle \mathbf{B}. \quad (60)$$

Since this effect is weak, we ignore neighbours effect on an ion<sup>11</sup>. We get the magnetization to be for  $N$  such atoms to be

$$\mathbf{M} = N\boldsymbol{\mu} = -\frac{NZe^2}{4m} \langle \rho^2 \rangle \mathbf{B} \quad (61)$$

using equation 28 we get an expression for the susceptibility

$$\chi = -\frac{NZe^2 \mu_0}{4m} \langle \rho^2 \rangle \approx 10^{-5} \quad (62)$$

Where the approximation in order to the get order of magnitude is done through approximating  $\langle \rho^2 \rangle \approx a_0^2$ , where  $a_0$  is the Bohr radius. A very low susceptibility indeed.

<sup>10</sup>Note that it's required to have that  $\text{div} \mathbf{A} = 0$  for this vector potential to be usable, otherwise our assumption that  $\langle \mathbf{p} \rangle$  is constant under the applied field doesn't hold.

<sup>11</sup>We can then also set  $\mathbf{B} = \mu \mathbf{H}$

### 3.4 New words

- Diamagnetism
- Paramagnetism
- Magnetic susceptibility -  $\chi$
- Magnetization -  $M$
- Macroscopic magnetic field within a material -  $H$
- Saturation magnetization
- Curie law
- Curie constant
- Quenching
- Crystal field

## 4 Magnetic Order

### 4.1 Introduction

### 4.2 The exchange interaction

### 4.3 Ferromagnetism

#### 4.3.1 The Weiss molecular field

#### 4.3.2 Calculation of ferromagnetic properties using the mean field theory

### 4.4 The Néel model of antiferromagnetism

### 4.5 Ferromagnetic Domains

#### 4.5.1 The energy and thickness of a Bloch wall

#### 4.5.2 Why do domains occur?

#### 4.5.3 Magnetization curves of ferromagnets

### 4.6 New words

- Magnetic order
- Ferromagnetism
- Bloch wall
- Mean field theory
- 
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## References

## A Appendix